

Figure 1.

Registry No.—1a, 25859-37-4; 1b, 37781-25-2; 1c, 22200-39-1; 1c N-oxide, 25907-81-7; 1d, 51794-47-9; 1d N-oxide, 51820-05-4; 2a, 42880-45-5; 2b, 37781-31-0; LiAlD₄, 14128-54-2.

References and Notes

- (1) This work was supported by the National Science Foundation (Grant GP-35429).
- (2) (a) W. E. Parham, K. B. Sloan, K. R. Reddy, and P. E. Olson, *J. Org. Chem.*, **38**, 927 (1973); (b) *ibid.*, **39**, 172 (1974).
- (3) The major product had the same *R_f* value as anti alcohol 2 (X = OH) but fluoresced with a different color on silica gel; however, the product was not further characterized.
- (4) (a) E. L. Eliel, *J. Amer. Chem. Soc.*, **71**, 3970 (1949); (b) A. Streitwieser, *ibid.*, **75**, 5014 (1953); (c) G. K. Helmkamp, C. D. Joel, and H. Sharnan, *J. Org. Chem.*, **21**, 844 (1956).
- (5) V. M. Micovic and M. L. Mihailovic, "Lithium Aluminum Hydride in Organic Chemistry," Izdacko Preduzece, Belgrade, 1955, pp 116-118.
- (6) B. L. Shapiro, J. R. Hlubucek, G. R. Sullivan, and L. F. Johnson, *J. Amer. Chem. Soc.*, **93**, 3281 (1971).
- (7) For a recent review on nmr shift reagents see A. F. Cockerill, G. L. O. Davies, R. C. Harden, and D. M. Rackham, *Chem. Rev.*, **73**, 553 (1973).
- (8) N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience, New York, N. Y., 1956, pp 88-89.
- (9) W. E. Parham, R. W. Davenport, and J. B. Biasotti, *Tetrahedron Lett.*, 557 (1969).
- (10) Use of hydrogen peroxide in acetic acid was avoided so as to minimize possible D-H exchange of benzylic protons. Cf. W. E. Parham and P. E. Olson, *Tetrahedron Lett.*, 4783 (1973).
- (11) W. E. Parham, R. W. Davenport, and J. B. Biasotti, *J. Org. Chem.*, **35**, 3775 (1970).
- (12) The hydride was used as an unfiltered slurry.

Carbenium Ion Rearrangements in the Alkylation of Tertiary Halides with Trimethylaluminum

Earl G. Melby

Union Carbide Corporation, Chemicals and Plastics,
Bound Brook, New Jersey 08805

Joseph P. Kennedy*

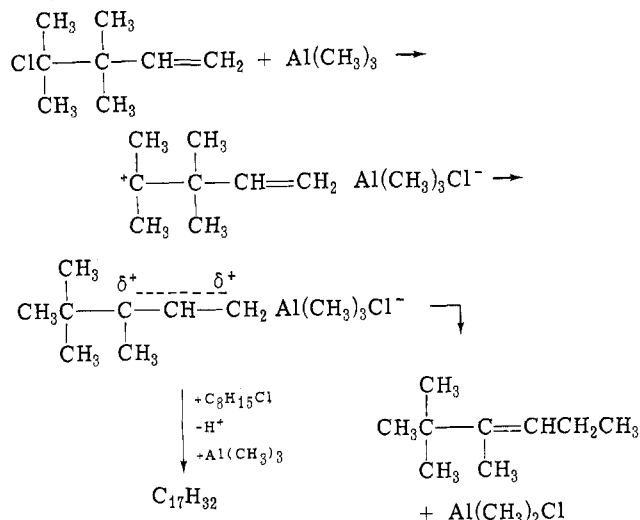
Institute of Polymer Science, The University of Akron,
Akron, Ohio 44325

Received March 25, 1974

In the course of our fundamental studies on cationic isomerization polymerization we were interested in the synthesis of 3,3,4,4-tetramethyl-1-pentene, which we hoped to obtain by methylating 4-chloro-3,3,4-trimethyl-1-pentene with Me₃Al. The rapid, quantitative methyl-

ation with Me₃Al of tertiary chlorines to quaternary carbons has recently been described.¹

Interestingly, instead of the desired product we obtained 2,2,3-trimethyl-3-hexene, most likely by the following route.

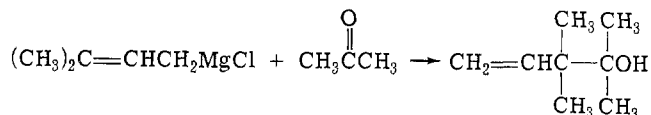


The initially formed carbenium ion rearranges to the more stable tertiary, allylic ion. This carbenium ion subsequently reacts with the counterion to give the thermodynamically more stable internal olefin.

In addition to 2,2,3-trimethyl-3-hexene, a second product of overall composition C₁₇H₃₂ was also obtained. While conclusive structural analysis could not be carried out, it is presumed that this product is a methylated dimer.

According to these findings allylic rearrangement by methide shift and dimerization is faster than methylation of the carbenium ion by the Me₃AlCl⁻ counteranion. The relatively slow methylation of carbenium ions with Me₃AlCl⁻ is important in cationic polymerization and might account for the formation of high molecular weight polymers by the faster propagation (dimerization) step.

The tertiary chloride used in the above scheme was prepared from the corresponding tertiary alcohol; no evidence for rearrangement during this step has been detected. The tertiary alcohol in turn was obtained by an unusual Grignard (rearrangement) synthesis found in our laboratory. Thus the reaction between γ,γ -dimethylallylmagnesium chloride and acetone yields 4-hydroxy-3,3,4-trimethyl-1-pentene. Evidently the internal C of the allylic system rather than the C bonded to the -MgCl reacts with the carbonyl function. Similar rearrangements during Grignard reactions of allylmagnesium halides have been described.^{2,3}



Experimental Section

General. Gas chromatographic analysis was carried out with an HP-5750 gas chromatograph. Molecular weights were determined using a Chromalytics MC-2 mass chromatograph. Nmr analysis was done using a Varian T-60 spectrometer. Microanalysis was done by Galbraith Laboratories, Knoxville, Tenn. Distillations were carried out using a Nester-Faust adiabatic spinning band column.

Synthesis of 4-Hydroxy-3,3,4-trimethyl-1-pentene. To synthesize this previously unknown alcohol, we adapted the procedure of Dreyfuss⁴ for the Grignard reaction. To 0.50 mol of magnesium turnings in 100 ml of ether was added γ,γ -dimethylallyl chloride (0.05 mol) in 25 ml of ether. After the reaction was proceeding vigorously, a solution of the remaining chloride (0.45 mol)

and acetone, 0.55 mol in 400 ml of ether, was added dropwise. The reaction was quenched using saturated aqueous NH_4Cl solution and filtered. After removal of the ether, distillation of the product mixture gave 4-hydroxy-3,3,4-trimethyl-1-pentene: 40% yield; bp $53\text{--}54^\circ$ (10 mm); nmr (CCl_4) δ 0.92 [s, 6 H, $\text{C}(\text{CH}_3)_2$], 1.02 [s, 6 H, $\text{C}(\text{CH}_3)_2$], 4.9–6.1 (m, 3 H, $\text{CH}=\text{CH}_2$). The aldol condensation of acetone accounted for the major by-product, diacetone alcohol.

Synthesis of 4-Chloro-3,3,4-trimethyl-1-pentene. To 4-hydroxy-3,3,4-trimethyl-1-pentene (25 g) was added 200 ml of concentrated HCl at 0° . The mixture was stirred for 30 min and the organic layer was removed and neutralized with K_2CO_3 . The product, 4-chloro-3,3,4-trimethyl-1-pentene, which previously has not been reported in the literature, was distilled: 100% yield; bp 55° (20 mm); mp $22\text{--}26^\circ$; nmr (CCl_4) δ 1.10 [s, 6 H, $\text{C}(\text{CH}_3)_2$], 1.48 [s, 6 H, $\text{C}(\text{CH}_3)_2$], 4.82–6.30 (m, 3 H, $\text{CH}=\text{CH}_2$).

Reaction of 4-Chloro-3,3,4-trimethyl-1-pentene with Trimethylaluminum. To a stirred solution of AlMe_3 (0.115 mol) in 200 ml of CH_2Cl_2 at 25° was added 4-chloro-3,3,4-trimethyl-1-pentene (0.10 mol) in 200 ml of CH_2Cl_2 . After 30 min, the reaction was quenched by slowly adding 50 ml of methanol and extracted with saturated aqueous potassium sodium tartrate solution. Removal of the CH_2Cl_2 yielded an organic phase containing two products which were separated by distillation. The lower boiling component was identified⁵ as 2,2,3-trimethyl-3-hexene: 69% yield; bp 56° (55 mm); mol wt 125.0 (calcd for C_9H_{18} , 126.2); nmr (CCl_4) δ 1.01 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 0.98 (t, 3 H, CCH_3), 1.55 (m, 3 H, CCH_3), 1.98 (m, 2 H, CH_2 -), 5.18 (t, 1 H, $-\text{CH}=\text{CH}_2$). The second component (31% yield) had bp 106° (3 mm), mol wt 238.0 (calcd for $\text{C}_{17}\text{H}_{32}$, 236.6). *Anal.* Calcd for $\text{C}_{17}\text{H}_{32}$: C, 86.5; H, 13.5. Found: C, 86.47; H, 13.50.

Acknowledgment. Partial financial support by the National Science Foundation (Grant GH-37985) is gratefully acknowledged.

Registry No.—Trimethylaluminum, 75-24-1; 4-hydroxy-3,3,4-trimethyl-1-pentene, 36934-19-7; γ,γ -dimethylallyl chloride, 503-60-6; acetone, 67-64-1; 4-chloro-3,3,4-trimethyl-1-pentene, 51751-72-5; 2,2,3-trimethyl-3-hexene, 51751-73-6.

References and Notes

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A Comment on the Acetoxythallation-Induced Lactonization of 2-endo-Norbornenecarboxylic Acids

Alexander McKillop* and Michael E. Ford

School of Chemical Sciences, University of East Anglia,
Norwich, England

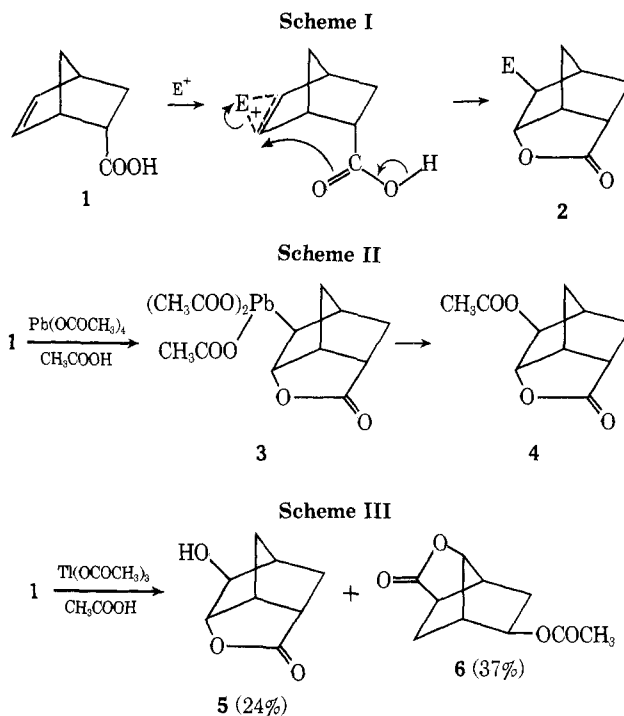
Edward C. Taylor*

Department of Chemistry, Princeton University,
Princeton, New Jersey 08540

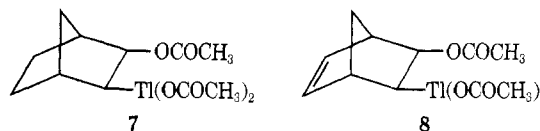
Received January 22, 1974

Electrophile-induced lactonization of 5-norbornene-2-endo-carboxylic acid (1) and related substrates is well known (Scheme I), and stable lactones 2 have been obtained when E is hydrogen,¹ halogen,² or acetoxymercury(II).³ Neighboring-group participation has also been invoked to account for the formation of 4 when 1 is oxidized with lead(IV) acetate (Scheme II).^{4,5} In this case, electrophile-induced lactonization presumably gives the oxymetalation adduct 3 as an unstable intermediate, and rapid conversion of 3 into 4 is fully consistent with the known lability of carbon-lead bonds in alkyllead(IV) triacetates.⁶

Oxidation of 1 with thallium(III) acetate has recently been reported by Moriarty and Gopal to give a mixture of 5 and 6 (Scheme III), formation of which was explained on



the basis of the sequence (i) neighboring-group participation during acetoxythallation; (ii) generation of a norbornylthallium(III) diacetate; and (iii) facile heterolysis of this latter species to give the corresponding carbonium ion from which 5 and 6 are ultimately derived.⁷ In principle this explanation is quite reasonable. Most oxythallation adducts are notoriously unstable, very few have ever been isolated, and their decomposition in solution is believed to involve heterolysis of the carbon-thallium bond and generation of carbonium ions.⁸ Nevertheless, we were surprised by Moriarty and Gopal's comment *vis à vis* Scheme III that "Attempts were made, to no avail, to isolate the proposed organothallium intermediate in the present examples." Some 10 years ago Pande and Winstein showed that treatment of norbornene and norbornadiene with thallium(III) acetate gave the *cis,exo*-acetoxythallation adducts 7 and 8 as relatively stable, isolable solids,⁹ and



we have confirmed these results on a number of occasions in our own laboratories. As there appeared to us to be no obvious reason why the oxythallation adduct of 1 should be significantly less stable than compounds 7 or 8, we have reinvestigated the reaction of 1 and some related compounds with thallium(III) acetate.

Oxidation of 1 with thallium(III) acetate in glacial acetic acid proceeded smoothly at room temperature to give the oxythallation adduct 9 in 88% yield as an easily handled, relatively stable, colorless, crystalline solid. The presence of the five-membered lactone ring was evident from the ir spectrum ($\nu_{\text{C}=\text{O}}$ 1780 cm^{-1}), while the nmr spectrum exhibited the expected large $^1\text{H}\text{--}^{203/205}\text{Tl}$ coupling constants characteristic of organothallium compounds (Table I).^{10,11} Similar treatment of the dicarboxylic acids 10 and 12 provided the analogous crystalline lactones 11 and 13 in virtually quantitative yield. As with compound 9, the ir spectra of 11 and 13 showed characteristic, strong lactone absorptions at $1780\text{--}1800\text{ cm}^{-1}$; the presence of the covalent carbon-thallium bond was again confirmed by nmr spectroscopy (Table I).